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Substrate/Buffer Layer Compounds in the Calcium Antimonate System for Growth of Epitaxial YBCO Films

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Using pulsed laser deposition (PLD), epitaxial thin films of Yttrium-Barium-Copper-Oxide (YBCO) have been grown on films of compounds in the calcium antimonate system, Ca_2MeSbO_6, where Me=Al, Ga, Sc, In, Y and La. Bulk targets of compounds were prepared from precursor oxides and carbonates using solid state reaction at temperatures between 1400 and 1500 °C. Epitaxial relationships were determined from x-ray diffraction data. All antimonates investigated demonstrated (*00l*) epitaxy and should support (*00l*) growth of YBCO. Dielectric constants and losses of bulk samples were measured using cavity perturbation techniques at x band. As reported, all antimonates exhibit low dielectric constants and low losses.

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SUBSTRATE/BUFFER LAYER COMPOUNDS IN THE CALCIUM ANTIMONATE SYSTEM FOR GROWTH OF EPITAXIAL YBCO FILMS

INTRODUCTION

Most superconducting microwave devices continue to be fabricated from epitaxial thin film structures deposited on single crystal substrates. The need for better lattice-matched, cubic, low dielectric constant and low microwave loss substrates/buffers continues [1]. While lanthanum aluminate ($LaAlO_3$) is a popular substrate, it is being challenged by lanthanum-strontium-aluminum-tantalate (LSAT). LSAT is a solid solution of 30 mole % $LaAlO_3$ and 70 mole % strontium-aluminum-tantalate (Sr_2AlTaO_6) [2,3]. LSAT overcomes some of the drawbacks associated with $LaAlO_3$. It is cubic, does not undergo a phase transition and has a slightly lower dielectric constant. $LaAlO_3$ puts high critical temperature superconducting (HTSC) films in compression, an advantage for brittle films with poor thermal expansion matches [4]. The lattice parameter for LSAT falls between that of the *a* and *b* parameters of $YBa_2Cu_3O_{7-\delta}$ (YBCO) and probably introduces less stress than $LaAlO_3$, providing an even greater advantage. Both the dielectric constant for $LaAlO_3$ (ε_r=24) and for LSAT (ε_r=22.5) [5] are relatively large. Thus an optimum substrate/buffer would be one with a much lower dielectric constant. We have previously investigated ordered perovskites of the alkaline-earth type A_2MeSbO_6, where A=Ba or Sr and Me is a trivalent ion often ordered on octahedral sites [6,7]. Because pentavalent ions have a smaller polarizability (Sb^{+5}=1.18±0.45 Å^3) [4], the dielectric constants for these compounds are much smaller than observed in $LaAlO_3$ or LSAT [5,7]. The polarizability of Ca^{2+} on A sites in perovskites is 30% smaller than Sr^{2+} and 100% smaller than Ba^{2+} [8]. Since Ca^{2+} is smaller than Ba^{2+} or Sr^{2+} a better opportunity is afforded for lattice matching to YBCO (*a*=3.82, *b*=3.89 and *c*=12.68 Å). Therefore, the investigation of compounds in the calcium antimonate system, Ca_2MeSbO_6, where Me=Al, Ga, Sc, In or a rare-earth was undertaken in search of a lattice matched, cubic perovskite with a low dielectric constant.

EXPERIMENTAL

Preparation of bulk targets of compounds in the system Ca_2MeSbO_6 were carried out using solid state reaction. Stoichiometric amounts of the precursors, 99.9% pure or better calcium carbonate ($CaCO_3$), aluminum oxide (Al_2O_3), gallium trioxide (Ga_2O_3), scandium oxide (Sc_2O_3), indium trioxide (In_2O_3), antimony trioxide (Sb_2O_3), rare-earth oxide (Re_2O_3) were ground together in a BC mortar until homogeneous. The powder was pressed into 2.54 cm discs and heated at 3 °C/min to 1100 °C, held for 15-20 hours and cooled to room temperature. The discs were ground to a powder <100 μm, pressed into 3.18 cm discs in a steel die, repressed isostatically at 344 MPa, ramped at 18 °C/hr, sintered between 1400 and 1550 °C for 20 to 60 hours, cooled to 100 °C at the same rate and removed from the furnace. If x-ray diffractometry

scans revealed the presence of a second phase, the discs were reground and the last step was repeated until a single phase was produced. Lattice parameters, Table 1, were determined by fitting the Nelson-Riley function to the x-ray diffraction peaks obtained from $\theta-2\theta$ x-ray scans from 15 to 155° 2θ using CuK_α radiation as the source [9]. Densities obtained using He gas pycnometry are compared with x-ray densities in Table 1. The bulk discs were employed for microwave measurements and as targets for pulsed laser deposition (PLD) of thin films. Microwave measurements of the real and imaginary parts of the dielectric constant were carried out at room temperature and 9.3 GHz. Details of this measurement may be found elsewhere [7]. For PLD, deposition parameters were a pulse repetition rate of 10 Hz, laser fluence of 1-2 J/cm^2, an oxygen pressure of 13.6 Pa and a heater block temperature of about 750 °C.

Table 1. Bulk Properties of Ca_2MeSbO_6 Compounds.

Compound	Lattice Parameter (Å)		Density (g/cm^3)		Dielectric Properties		
	Measured	Literature	X-ray	Measured	Theoretical Constant	Measured Constant	Loss Tangent (10^{-3})
Ca_2AlSbO_6	Pseudo-Cubic $a = 7.607$ Orthorhombic $a = 5.321$ $b = 5.368$ $c = 7.540$	Cubic $a = 3.81$	5.20	4.51	11.3	9.5	6
Ca_2GaSbO_6	$a = 7.621$		4.60	4.05	9.8	5.4	9.0
Ca_2ScSbO_6	Pseudo-Cubic $a = 7.800$	Cubic $a = 3.92$	4.79	4.80	11.3	13.3	<1
Ca_2InSbO_6	$a = 7.992$	$a = c = 3.968$ $b = 3.967$ b = 91° 31"	5.36	5.16	9.0		
Ca_2YSbO_6	Pseudo-Cubic $a = 8.030$	$a = c = 4.087$ $b = 4.028$ $b = 92°\ 05"$	4.96	4.69	9.9		
Ca_2LaSbO_6	Pseudo-Cubic $a = 8.148$	$a = c = 4.087$ $b = 4.085$ $b = 91°\ 47'$	5.36	4.86	12.4		
LCAS	Cubic $a = 7.561$		4.75	4.79	15.3	7.1	2.5

RESULTS

The Ca_2MeSbO_6 compounds where Me = Al, Sc, In, Cr, Fe, Mn and rare earth containing compounds were first prepared by Fesenko et al. [10]. No microwave properties were reported. They found that the Al, Sc, Cr, Fe and Mn containing compounds were cubic and the In compound was monoclinic. Their lattice parameters are given in Table 1. The rare-earth compounds were found by them to be monoclinic.

We find that Ca_2InSbO_6 is the only cubic compound in the series in contradiction to the observation of Fesenko et al. [10]. Ca_2AlSbO_6 was found to be orthorhombic, not cubic, although the distortion from cubicity is small. The Ca_2GaSbO_6 and Ca_2ScSbO_6 are also not cubic; however, the distortion from cubicity is large. We find Y and La compounds are not cubic in agreement with Fesenko et al. No attempt to index Ga, Sc, Y or La was undertaken. The observed dielectric constants of these materials confirm the model [11], based on ionic polarizabilities, that dielectric constants are low. The Ca_2MeSbO_6 thin films exhibit an (00*l*) epitaxy on (00*l*) oriented YBCO films and an (00*l*) epitaxy on (00*l*) oriented LSAT and $LaAlO_3$ single crystal substrates (Table 2). Therefore, all the antimonates investigated should support epitaxial (00*l*) growth of YBCO. Ca_2AlSbO_6 would put YBCO films grown on it in compression. Ca_2GaSbO_6 would put the *a* parameter in tension and be almost an exact match for the *b* parameter of YBCO. All of the other antimonates place YBCO films in tension.

Table 2. Film Properties of Ca_2MeSbO_6 Compounds.

COMPOUND	OBSERVED REFLECTIONS
Ca_2AlSbO_6/(00*l*)YBCO/(100)LSAT	002, 004, 006
Ca_2AlSbO_6/(100)LSAT	002, 004, 006
Ca_2AlSbO_6/(211)GGG	420, 442, 642
Ca_2AlSbO_6/(100)$LaAlO_3$	002, 004, 006
Ca_2GaSbO_6/(00*l*)YBCO/(100)LSAT	002, 004, 006
Ca_2GaSbO_6/(100)LSAT	002, 004
Ca_2GaSbO_6/(211)GGG	420
Ca_2GaSbO_6/(100)$LaAlO_3$	002, 008
Ca_2ScSbO_6/(00*l*)YBCO/(100)LSAT	002, 004, 006
Ca_2ScSbO_6/(100)LSAT	002, 004, 006
Ca_2ScSbO_6/(100)$LaAlO_3$	002, 004, 006
Ca_2InSbO_6/(00*l*)YBCO/(100)LSAT	002, 004, 006, 008
Ca_2InSbO_6/(100)LSAT	002, 004
Ca_2YSbO_6/(00*l*)YBCO/(100)LSAT	002, 004
Ca_2YSbO_6/(100)LSAT	002, 004
Ca_2LaSbO_6/(00*l*)YBCO/(100)LSAT	004
Ca_2LaSbO_6/(100)LSAT	004, 008
Ca_2LaSbO_6/(100)$LaAlO_3$	002, 004, 008
LCAS/(00*l*)YBCO/(100)LSAT	002, 004

Since the most useful antimonates are not cubic, an attempt was made to synthesize a cubic antimonate with a closely matching lattice constant and reduced dielectric constant by preparing a solid solution between Ca_2AlSbO_6 and $LaAlO_3$. A 75 mole% Ca_2AlSbO_6 - 25 mole% $LaAlO_3$ solid solution (LCAS) was prepared as described in the experimental section. The results are given in Table 1. Not only was a cubic compound obtained but one that places YBCO in compression and provides a dielectric constant smaller than either $LaAlO_3$ or LSAT.

CONCLUSION

Microwave compatible, low dielectric constant, low loss, cubic lattice matching materials for use as HTSC substrates/buffer layers are possible using solid solutions involving antimonate perovskites.

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